

Preparation and Fabrication of Aromatic Polyimides

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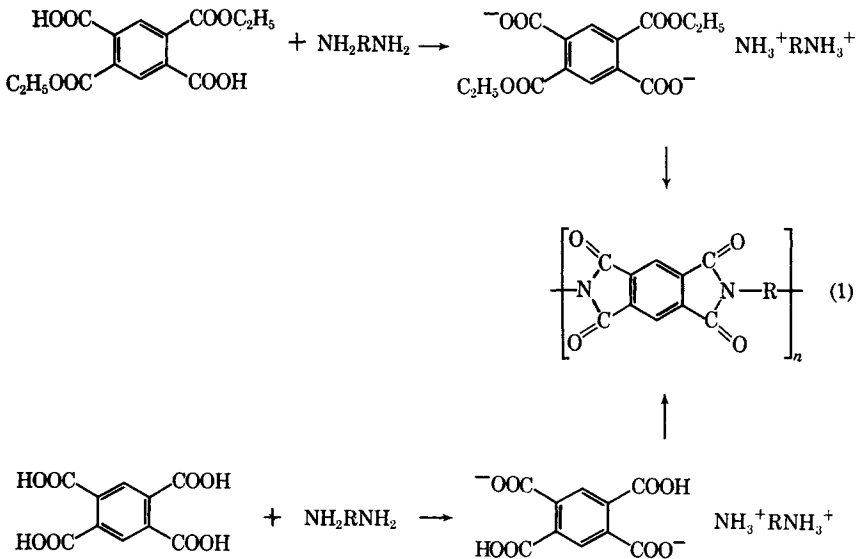
Synopsis

Aromatic polyimides were prepared from pyromellitic dianhydride and a number of aromatic diamines. The effect of certain variables on the polymerization to, and the degradation of, the intermediate polypyromellitic acids was studied, and a previously unrecorded reaction intermediate was isolated and identified. From these studies the conditions necessary to obtain high molecular weights were defined. Techniques were developed for the fabrication of satisfactory films and moldings.

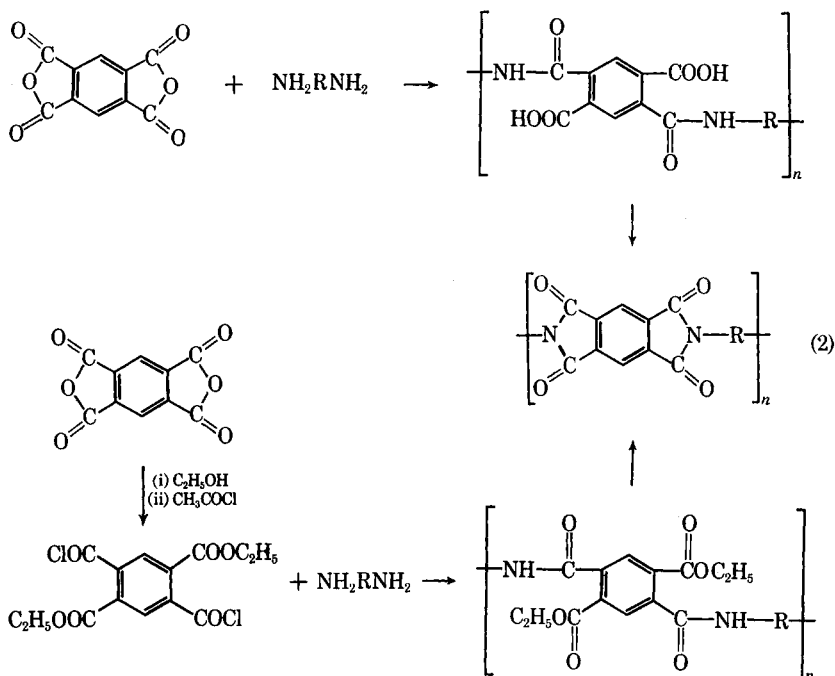
INTRODUCTION

Polyimides are one of a growing number of aromatic and heterocyclic polymers recently developed in the search for structural stability at elevated temperatures. Depending on the environment and the exposure time, useful service lives may be obtained in the region of 300-500°C.¹

The fundamental reactions for synthesis of the imide ring have long been known. In the post-war period these were applied to give aliphatic polymers via nylon-type condensation routes from aliphatic diamines with both aliphatic and aromatic tetracarboxylic acids and their esters.²⁻⁴



The polyimides formed were soluble and fusible and were suggested for use in injection-molding processes. These reaction routes proved to be unsatisfactory when attempts were made to prepare fully aromatic polyimides because of the precipitation of low molecular weight "brickdusts" at an early stage in the reaction. As a result of these failures, solution polymerization methods were developed by various workers.⁵⁻¹³ Related reactions have also been described for the preparation of amide-imide copolymers.^{10,14}



In the course of the preparation of polyimides of varying structure for thermal stability determinations, the polymerization reaction was studied in some detail and the formation of a prepolymer complex noted, which has not previously been reported. The conditions necessary for the formation of high molecular weight polymer were confirmed and techniques developed for producing satisfactory films and moldings.

EXPERIMENTAL

Reagents

Pyromellitic Dianhydride (PMDA). This was purified via complex formation with anisole⁹ to give a pure white material melting at 286°C . This method was found to be preferable to either vacuum sublimation from phosphorus pentoxide or recrystallization from acetic anhydride.

Two spot tests were used to detect small degrees of hydrolysis in PMDA.

(1) A few crystals of PMDA were added to dry anisole in a flamed semi-micro test tube and the solvent heated to boiling. The formation of turbidity in the hot yellow solution indicated that traces of acid were present.

(2) A few crystals of PMDA were added to dry tetrahydrofuran in a flamed test tube and dissolved by shaking. Two drops of pure dry pyridine were then added. The immediate formation of a white precipitate indicated the presence of pyromellitic acid. The dipyrindinium salt could be filtered off, dried, and estimated gravimetrically.

Diamines. These were purified by recrystallization from benzene or from an alcohol-tetrahydrofuran mixture, followed by prolonged vacuum drying over phosphorus pentoxide.

Solvents. Dimethylformamide and dimethylacetamide were fractionally distilled from phosphorus pentoxide at 20 and 30 mm. Hg., respectively, and stored over cobalt-free silica gel dried at 250°C. Other solvents used, e.g., tetrahydrofuran, were first dried and then distilled.

Polymerization Procedures

A number of solution polymerization methods were investigated and these may be classified as follows: homogeneous mixing (both components reacted in solution): (Ho1) dianhydride solution run into the diamine solution, (Ho2) diamine solution run into the dianhydride solution, (Ho3) both solutions mixed simultaneously, or added alternately; heterogeneous mixing (one or more components added as solid): (He1) solid dianhydride added to diamine solution, (He2) solid diamine added to dianhydride solution, (He3) both solids dissolved simultaneously or added alternately.

These methods all resulted in rapid polymerization to the poly(amic acid); the products were evaluated by viscosity determination, infrared spectra measurements and observations of film-forming properties.

By dissolving both components in dry tetrahydrofuran instead of dimethylformamide or dimethylacetamide, it was possible to modify the Ho3 type polymerization to give simultaneous formation and precipitation of poly(amic acid). The course of the reaction was similar to that followed in solution polymerization, although it was more affected by differences in reactivity among the diamines.

This polymerization process proved to be particularly useful for the preparation of polymer intermediates free from the usual tightly bound solvents. Both the poly(amic acids) and the amine salt analog formed by using pyromellitic acid instead of the dianhydride could be obtained in this manner as light-colored, finely divided, hygroscopic powders. It was then possible to observe the effect of heat, pressure, and chemical reagents on these products without interference from the plasticizing effects of trace amounts of dimethylformamide or dimethylacetamide. This proved to be an important step in the preparation of a molding powder. The selectivity of the precipitation reaction also made it possible to identify stages in the polymerization that were masked in more powerful solvents.

Viscosity Measurements

Viscosity measurements were carried out at two levels of accuracy.

(1) Relative measurements were made at 20°C. on casting solutions of 10% solids content. These measurements were made by using pipets of 2–10 ml. capacity with gage marks equidistant above and below the bulb. Flow times were measured without accurate temperature control and were converted approximately to centipoises by comparison with a range of standard silicone oils. This type of measurement was useful for studying the effects of mixing technique, stoichiometric ratio, impurities, and solution degradation.

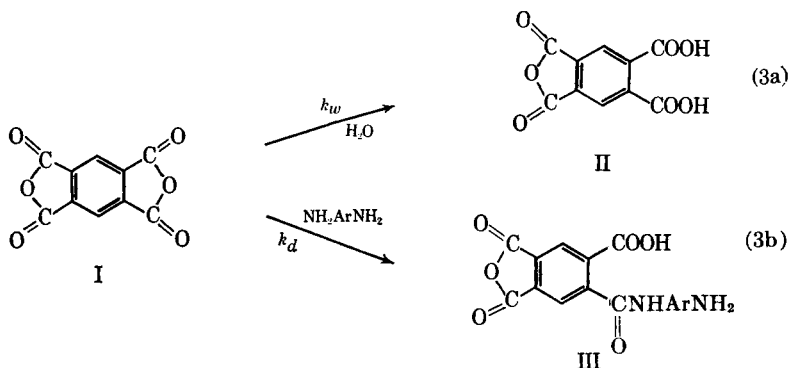
(2) Accurate measurements were made at $30 \pm 0.05^\circ\text{C}$. on solutions of approximately 0.5% solids content, to give inherent and reduced viscosity values.

RESULTS AND DISCUSSION

Formation of Poly(amic Acids)

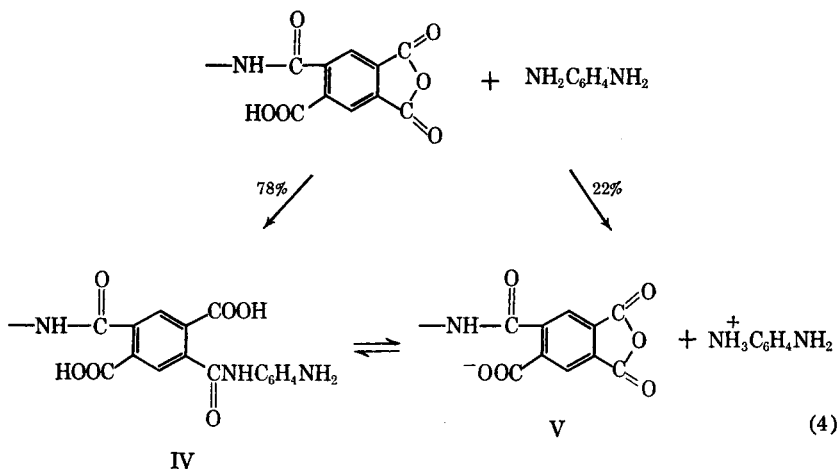
The viscosity of the poly(amic acid) solution produced was very dependent on the mixing technique (Fig. 1), the highest values being obtained when the PMDA was added as a solid (processes He1 and He3). Maximum viscosities were obtained with the PMDA in 0.4–0.5% excess of the equivalent amount, this being about one tenth of the excess reported by Bower and Frost.¹⁰ The concentration at which the polymerization was effected also had a marked influence on the viscosity attained, the inherent viscosity of a 0.5% solution increasing linearly with increase in solids content at polymerization in the range 0–10%. It was observed in determining inherent viscosities in dimethylformamide, that at concentrations less than about 0.3 g./100 ml., there were sharp deviations to higher values. This effect has been attributed by Flory¹⁵ to the effect of ionic groups in the polymer repeating unit, thus suggesting that appreciable ionization of the *o*-carboxylic acid group of the poly(amic acid) may occur in dilute dimethylformamide solutions. Bower and Frost¹⁰ observed a similar phenomenon with diaminodiphenyl ether poly(amic acids) in dimethylacetamide, but only when triethylamine was added. These differences may be caused by greater dissociation of the poly(amic acids) in dimethylformamide compared with dimethylacetamide.

The results show, in agreement with other workers,¹⁰ that if the PMDA is dissolved before reaction, much lower molecular weights are attained, the effect being greater for more dilute solutions. These facts can be explained in terms of competitive aminolysis and hydrolysis reactions for the PMDA, the crucial difference between the heterogeneous and homogeneous mixing methods being that in the former aminolysis and hydrolysis reactions are in competition, whereas in the latter hydrolysis may occur freely before aminolysis is initiated.



From simple measurements of the rate at which heat was liberated during reactions (3a) and (3b) it was found that k_d/k_w was approximately 5, i.e., with the diamine present in large excess very little hydrolysis would occur.

Wraslido et al., from a study of the condensation of *m*-phenylenediamine and PMDA in dimethylacetamide, concluded that an amine salt structure could exist in equilibrium with the poly(amic acid) [eq. (4)].¹⁶



Approximate measurements of the enthalpy change for these two reactions were made, and that for IV was greater by approximately 13 kcal./mole. The position of equilibrium given by Wraslido requires that the free energy difference should be not greater than 1 kcal./mole. As no data are available on the entropy changes involved, the enthalpy change alone cannot be taken as proving the unlikelihood of the route leading to V. However, infrared spectra of pure poly(amic acids) from diaminodiphenylmethane and diaminodiphenyl ether, both before and after aging, show no measurable anhydride bands.

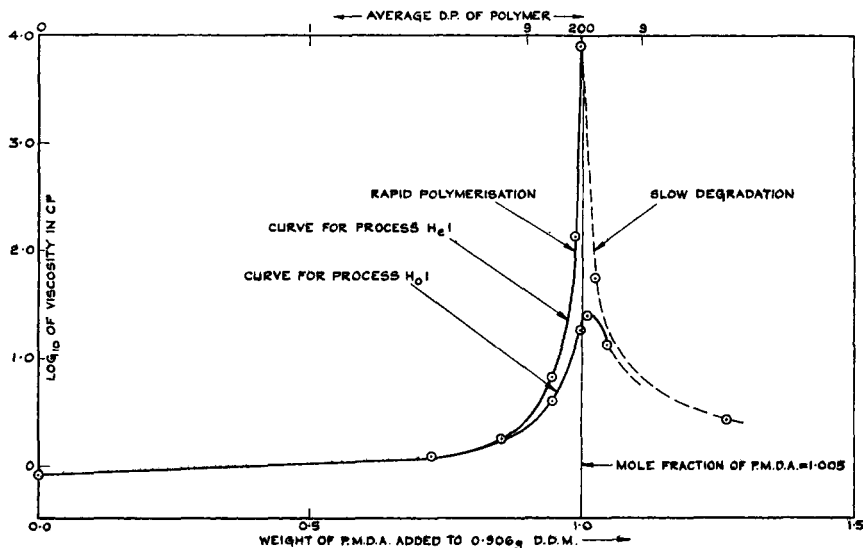


Fig. 1. Effect of component ratio and polymerization method on viscosity of 10% solutions of diaminodiphenylmethane poly(amic acid) in dimethylformamide at 20°C.

Degradation of Poly(amic Acid) Solutions

As described previously,¹¹ the poly(amic acid) solutions once formed degraded, the rate being dependent on the temperature and the environment, the presence of moisture being especially deleterious (Fig. 2 and Table I). The decrease in viscosity was accompanied by a progressive discoloration that was photooxidative in nature and probably involved

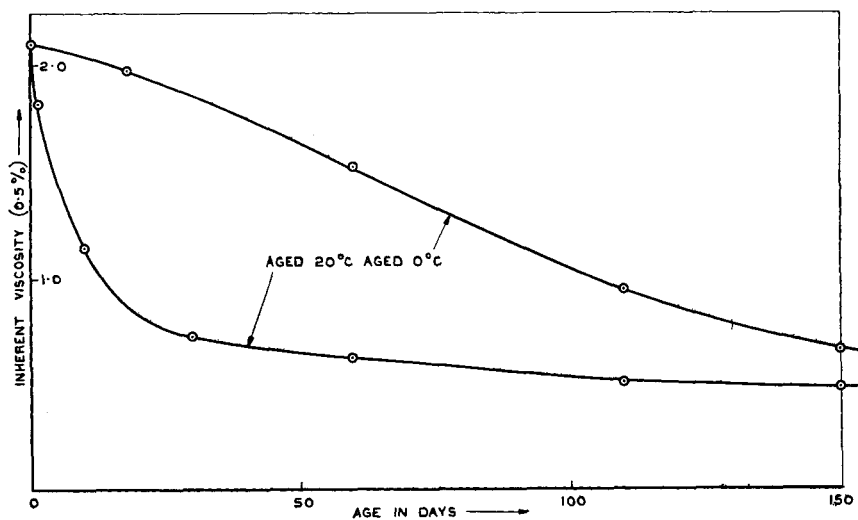


Fig. 2. Effect of time and temperature on degradation of 10% solutions of diaminodiphenylmethane poly(amic acid) in dimethylformamide.

TABLE I
Effect of Aging Conditions on the Degradation of Poly(amic Acid) Solutions^a

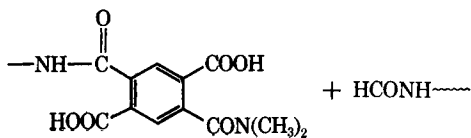
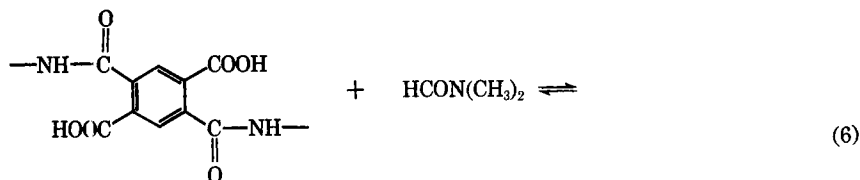
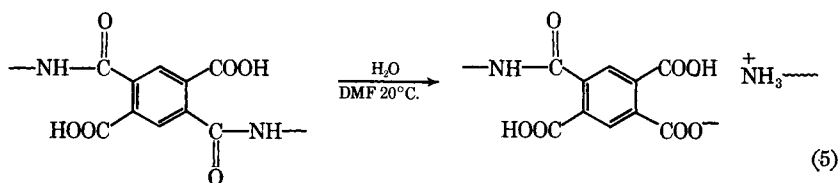
Temperature, °C.	Exposed to light	Exposed to air	Exposed to moisture	Viscosity after 1 month	Color of solution
20	No	No	No	0.71	Straw yellow
20	Yes	No	No	0.68	Straw yellow
20	No	Yes	No	0.67	Light amber
20	Yes	Yes	No	0.52	Dark amber
20	Yes	No	5% water added	0.25	Straw yellow
0	No	No	No	1.90	Straw yellow
0	No	Yes	No	1.86	Straw yellow

^a Sample of poly(amic acid) from diaminodiphenylmethane and pyromellitic dianhydride polymerized by method He1 at 10% solids content in dimethylformamide under anhydrous conditions. The initial inherent viscosity for a 0.5% solution at 30°C. was 2.05.

After 8 months a sample maintained at 20°C. in the presence of light and air had gelled and was dark amber in color.

oxidation of liberated amine groups. Poly(amic acid) solutions derived from *p*-phenylenediamine and to a lesser extent from *m*-phenylenediamine were an exception to the general rule, as gelling occurred over a period of days. This was also observed for a poly(amic acid) solution from diaminodiphenylmethane after exposure to the atmosphere for several months. In the latter case, appreciable conversion (10–15%) to imide had occurred, as evidenced by infrared spectra. There was no indication of this happening in the gelled material from *p*- and *m*-phenylenediamine.

Hydrolytic attack on the amide bond could occur to give groups with an amine salt structure, and because of the ability of dimethylformamide to solvate these groups [eq. (5)], the chain cleavage would be shown by a decrease in viscosity.



Water could be introduced with the reagents or would be produced over a time period, through the spontaneous imidization reaction.

It is also possible that the degradation could occur by an exchange reaction with the solvent [eq. (6)].

Such a process would also account for the dependence of molecular weight on the solids content during polymerization and the difference in rates of degradation observed for dimethylformamide and dimethylacetamide solutions.

Cyclization to Polyimides

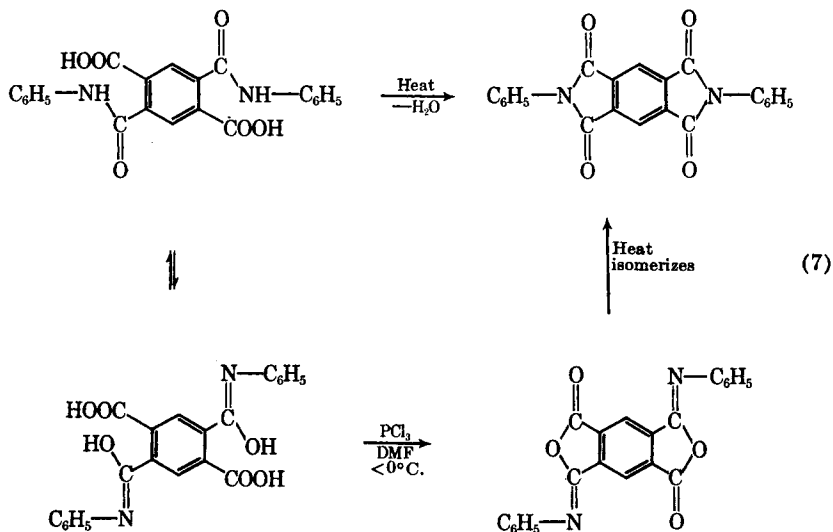
The conversion of poly(amic acids) to the corresponding polyimides was effected by the use of heat or chemical dehydrating agents. Whereas cyclization of the poly(amic acids) was virtually complete after refluxing in dimethylformamide solution at 150°C. for 10 min., the solvent-free powders obtained from tetrahydrofuran polymerization required several hours at 180°C. to attain the same state, showing that the solvent served to accelerate the process.

TABLE II
Effect of Cyclizing Conditions on Reaction Products

Amic acid	Temperature, °C.	Reagents	Phase	Products
Poly(amic acid) from diaminodiphenylmethane and PMDA	150	—	Dimethylformamide solution	Imide
	180	—	Powder from tetrahydrofuran preparation	Imide
	150	Pyridine	Dimethylformamide solution	Imide
	20	Pyridine + acetic anhydride	"	Imide
	<0	Phosphorus trichloride	"	Imide + isoimide
	<0	"	Tetrahydrofuran suspension	Imide
Amic acid from aniline and PMDA	150	—	Dimethylformamide solution	Imide
	20	Pyridine + acetic anhydride	"	Imide
	<0	Phosphorus trichloride	"	Isoimide
	<0	Phosphorus trichloride + pyridine or triethylamine	"	Isoimide
	<0	Phosphorus trichloride	Tetrahydrofuran suspension	Imide

Because of their basicity and lack of reactive groups, tertiary amines could be used with the conventional solvents to catalyze the thermal cyclization reaction, but to obtain rapid cyclization in the region of room temperature it was necessary to have a dehydrating agent present to give a favorable energy balance. The use of 50/50 mixtures of acetic anhydride with pyridine or β -picoline for this purpose have been reported,^{5,12} but phosphorus trichloride alone or with either pyridine or triethylamine yielded some unexpected products. The use of these reagents on amic acids in cooled dimethylformamide solutions provided a general route to the isoimides, giving yields of 60–70% with both amic acids or "model compounds" and with poly(amic acids) (Table II). The isoimides were generally brilliant yellow to orange powders with two strong characteristic infrared absorptions at 1800 and 1710 cm^{-1} , attributed to stretching frequencies of the strained >C=O and >C=N —structures, respectively.

The isoimides were unstable, rapidly reverting to the pure imide on heating [eqs. (7)]. The anhydride ring reacted with aromatic amines to provide a synthetic route to the unstable aryl tetraamides of pyromellitic acid. These readily expelled the more labile amine component to give the normal pyromellitimides.



Color Reactions and Complex Formation

Detailed examination of the origin of the transient colorations observed at the start of the polymerization provided evidence of the existence of a prepolymer reaction intermediate, which could under certain circumstances be isolated as a stable crystalline complex of characteristic color.

The initial coloration depended on the diamine or amine used and the method or rate of reacting. It was generally most noticeable when equimolar solutions of reagents were mixed, a uniform intense color being

TABLE III
 Diamine and Monoamine Complexes with PMDA

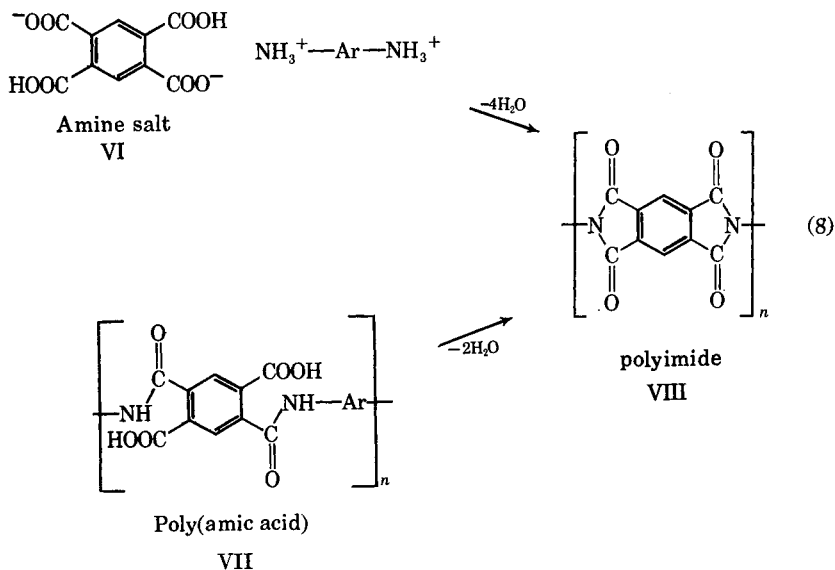
Amine	Color of complex		Decomposition temperature of complex, °C.
	In solution	Solid	
<i>m</i> -Phenylenediamine	Dark red	—	<<20
<i>p</i> -Phenylenediamine	Dark red	—	<<20
Benzidine	Dark red	—	<<20
4,4'-Diaminodiphenylmethane	Dark red	—	<<20
4,4'-Diaminodiphenyl ether	Red	—	<<20
4,4'-Dimethylaminodiphenylmethane	Red	—	Slow at 20
4,4'-Diaminodiphenylsulfone	Orange	Light yellow	Slow at 40
4,4'-Diaminobenzophenone	Orange	Light yellow	Slow at 40
3,3'-Dichlorobenzidine	Dark red	Dark green	Slow at 60
2,2',6,6'-Tetrachlorobenzidine	Dark red	Dark red	Very slow at 60
Octafluorobenzidine	Light yellow	Colorless	Very slow at 60
Aniline	Red	—	<<20
Monomethylaniline	Red	—	Slow at 20
Dimethylaniline	Dark red	Dark red	—

produced in both dimethylformamide and tetrahydrofuran. In the latter case the color faded as the polymer precipitated, suggesting that its formation preceded the actual polymerization. This was confirmed by the use of *N*-dimethylaniline as a "blocked" reagent, and by the use of very weakly basic diamines that gave stable colored complexes as a precursor to the poly(amic acid). The weaker solvent power of tetrahydrofuran was an advantage with these compounds, enabling the complexes to be crystallized from solution. The results obtained with a number of mono- and diamines are summarized in Table III. The compounds were similar to the charge-transfer complexes studied by Tolland et al.^{17,18} having a 1:1 ratio of constituents and the infrared spectra of the individual components. Measurements of solution conductivity also showed a transient high value which rapidly decayed.

In general the stability of the complex decreased with increasing basicity of the amine, although this could be overruled by steric factors introduced by *N*-substitution. In dimethylformamide, the formation of a stable complex was indicated by a persistent coloration and failure to obtain an increase in the solution viscosity. The formation of a prepolymer intermediate susceptible to hydrolysis and oxidation could account for the failure of the less basic diamines to yield high molecular weight polymers. This was particularly true of diaminobenzophenone, which reacted with PMDA in dimethylformamide to give a persistent orange coloration and a slow rise in viscosity to a low value. In tetrahydrofuran a similar coloration persisted, and no polymer was obtained until the solution was heated to 40°C., when a gelatinous precipitate of the poly(amic acid) formed.

Diamines such as 3,3'-dichlorobenzidine, 2,2',5,5'-tetrachlorobenzidine, and octafluorobenzidine also only gave poly(amic acids) as precipitated powders on refluxing tetrahydrofuran solutions.

As pointed out earlier, ionic salt groups were formed instead of covalent amide bonds, as a result of hydrolytic attack on either the PMDA or poly(amic acid) in solution. Although this resulted in low molecular weight products it was found by elemental analysis and infrared studies that the polyimide structure was obtained from the amine salt (VI), although more slowly than from the *o*-carboxylamide (VII). Both were in the form of solvent-free powders isolated from tetrahydrofuran solutions.



Some evidence for the mechanism of cyclization of these groups was provided by distinctive color reactions observed with amine salts prepared from diaminodiphenylmethane under specific conditions. The color reactions were obtained with both the pure amine salt and with highly degraded poly(amic acid), providing further evidence that the same structure occurred in both compounds.

Photochromic Effect. An intense purple coloration formed on the surface of the dry solids when these were exposed to light. This occurred at room temperature, was irreversible in the dry state, but disappeared on treating the solids with solvents or reactive fluids.

Thermochromic Effect. An intense purple coloration appeared on heating dilute solutions in dimethylformamide. It disappeared on cooling, but slowly faded to an amber tint on prolonged heating.

Amine salts obtained from diamines other than diaminodiphenylmethane were examined for these effects, but only salts from diaminodiphenylether showed similar but weaker colorations. Apart from this lack of generality, the color reactions were very similar to those associated with the diaminodiphenylmethane charge-transfer complex. Both effects could be attributed to the dehydration of pyromellitic acid, probably catalyzed by the diamine, to yield the dianhydride associated with the diamine as the charge-

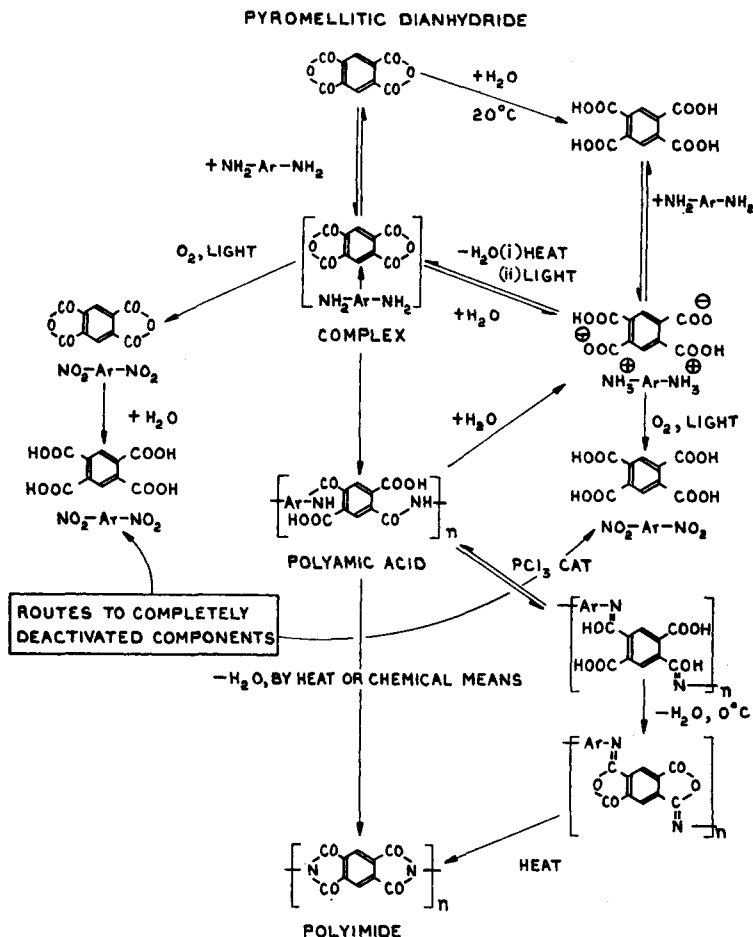


Fig. 3. Complete reaction scheme for polyimide formation.

transfer complex. The persistence of the coloration in the solid state suggested that the functional groups were locked in an unfavorable position for reaction, whereas solution freed them and allowed aminolysis to occur.

The above conclusions may be summarized in the complete reaction scheme showed in Figure 3.

FABRICATION OF POLYIMIDES

Film-Casting Techniques

A relatively small number of solvents have the specific properties required to give true solutions with the polyamic acids. These solvents are not inert dispersants, but interact with the polyamic acids in various ways. Such effects as the viscosity deviations in dimethylformamide (attributed to ionization of carboxyl groups) and the general catalysis of the cyclization

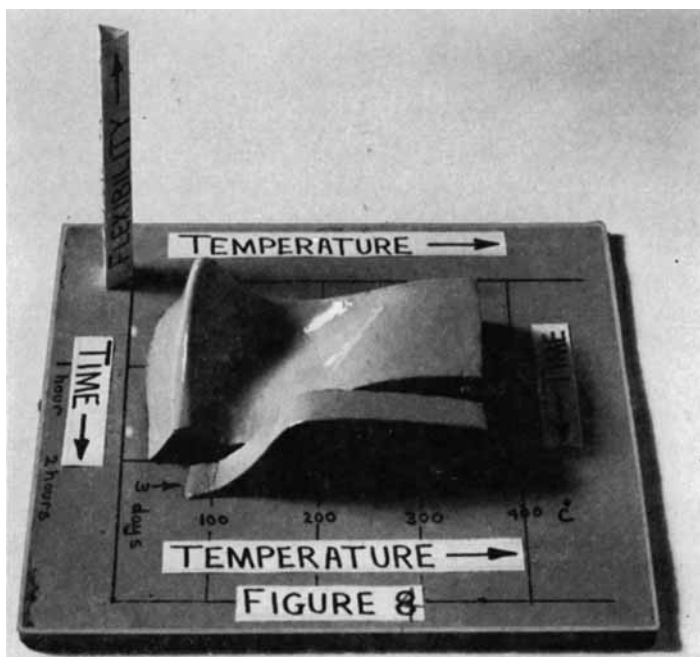


Fig. 4. Model demonstrating changes in flexibility during the film casting process.

reaction are of this type. In particular, the strong association between dimethylformamide or dimethylacetamide, and the poly(amic acid), together with the high boiling point of these solvents results in typical plasticization effects. It was possible to obtain cast films of the poly(amic acid) containing 10–20% solvent, which were clear, flexible, and had a high tear strength.

Precipitation of the polymer from dimethylformamide with a wide range of nonsolvents resulted in the separation of a rubbery phase containing a high proportion of dimethylformamide. Because of the physical state of the precipitate, and the strong association between polymer and solvent, it was impossible to remove the last traces of solvent without modifying the structure of the polymer, i.e., it was necessary to use either repeated washing with hot water, with attendant hydrolysis, or to use heat, with resultant cyclization to the polyimide. However, by use of the tetrahydrofuran polymerization process the poly(amic acid) was obtained as a fine precipitate, which could easily be stripped of absorbed tetrahydrofuran by extraction with ether or chloroform. The addition of water or typical poly(amic acid) solvents to the tetrahydrofuran "slurry" produced complete solution via coagulation of the precipitate. As little as 4% water in the solvent mixture was sufficient for this compared with approximately 50% of dimethylformamide. The addition of a large excess of water resulted in reprecipitation. Films of an inferior quality could be cast from these water-tetrahydrofuran solutions, but the process was complicated

by precipitation as the relative water content rose. When fully cured, these films were dark and rather brittle.

Small amounts of chloroform blocked the effect of water on the poly(amic acid) and would either prevent the deliquescent behavior of tetrahydrofuran slurries or precipitate the polymer from the resulting viscous solutions.

The properties of the cast films depended on the nature of the cure cycle. Figure 4 shows a model prepared to correlate the effects of temperature and time on flexibility during casting. It was derived from curves obtained for a poly(amic acid) of inherent viscosity, approximately 1.0, prepared from diaminodiphenylmethane and PMDA in dimethylformamide solutions of 10% solids content; but was typical for polyamic acids of this viscosity value. The flexibility was qualitatively assessed by observing the creasability of films 0.002–0.003 in. thick.

The initial high peak was due to the formation of plasticized poly(amic acid). It was not obtained with solutions of low inherent viscosity. The flexibility deteriorated with temperature and time because of solvent loss, cyclization and degradation processes.

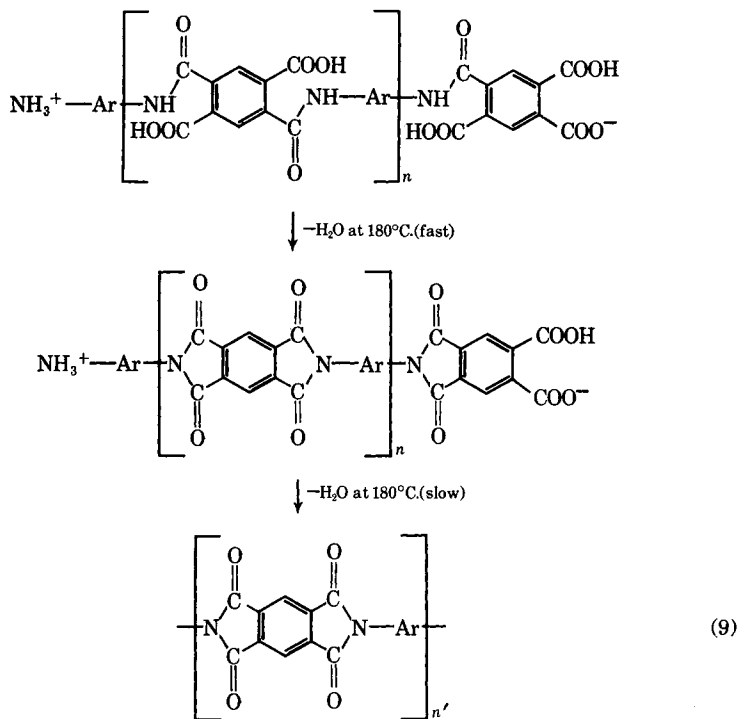
The loss in properties when the film, during formation, was subjected to a steady rise in temperature depended on the initial viscosity of the solution, the thickness of the film produced, and the rate of temperature rise. Thin films which could be cast rapidly were generally superior to thicker sections prepared from the same sample of poly(amic acid). The increased ratio of volume to surface area of the thicker sections, aggravated by "skinning" at the surface, resulted in two principal deleterious effects: (1) water liberated in the cyclization reaction was contained so that chain hydrolysis could occur; (2) The rate at which solvent could be removed was similarly restricted. As a result, cyclization could overtake solvent evaporation, with the formation of a precipitate of polyimide beneath the surface film; consequently sections thicker than 0.004–0.005 in. could not be prepared by the casting process. These effects could be mitigated to some extent by chemical cyclization of the cast poly(amic acid) films by using acetic anhydride–pyridine mixtures at 60–70°C., both the water of cyclization and the residual solvent being removed in this process.

When thermal cyclization was used, prolonged heating in the region of 100–150°C. produced irreversible deterioration of the cast film, but at higher temperatures there was a steady improvement in properties till the onset of oxidation of the polymer backbone above 400°C. As shown by Figure 4, the time required for this improvement in properties varied between several days at 180°C. to a few minutes at 400°C. The discontinuity, representing a lapse of several days, shows the long-term aging effects.

The observed "gap" in the flexibility of cast films between the stages at which they were plasticized poly(amic acids) and fully cured polyimides was a crucial factor in film casting. At this point films cast from poly(amic acids) of intermediate viscosity were found to craze badly under the stresses set up by loss of solvent and cyclization. Similar effects were ob-

served after immersion in acetic anhydride-pyridine mixtures. It was possible to obtain intact films by stripping them from the casting plates at the poly(amic acid) stage, suspending the films so that shrinkage could occur freely on curing at 150–180°C., and then curing these very brittle films at 300–400°C. to give complete conversion to the flexible polyimide. The problem could be overcome with polymers obtained from the more tractable diamines by preparing solutions with inherent viscosities in the range 2.0–2.5. In this case the products obtained at 180 and 400°C. were light yellow, tough, flexible films.

An adequate qualitative model of the flexibility changes is provided by the reaction scheme shown in eqs. (9).



In this reaction n is limited by chain termination during polymerization and n' depends on subsequent amine salt condensation. The two-stage nature of the process was confirmed by comparing the rates of cyclization of the polyamic acid and the 100% amine salt from diaminodiphenylmethane by isothermal weight loss at 180°C. in air. These reactions could be used to account for the differences observed during the fabrication of films from polyamic acids of different inherent viscosities (Fig. 5).

Solutions of Inherent Viscosity < 0.2 ($n < 10$). This low value of n gave a relatively high proportion of ionic endgroups. Besides the poor mechanical properties resulting from low molecular weight, the ionic endgroups provided points of high polarity, resulting in films that were brittle

and adhesive in the intermediate stage of the curing process. These samples showed no improvement on heating to 400°C.; in fact, they discolored and degraded. This was attributed to irreversible side reactions, probably involving amine oxidation and reaction with the solvent.

Solutions of Inherent Viscosity 0.2-1.0, ($n = 10-100$). These had a lower proportion of ionic groups and gave a flexible film of the poly(amic acid) while plasticized, deteriorating to a brittle film in the intermediate stage. Above 180-200°C. the rate of endgroup condensation became appreciable, and strong flexible films were finally obtained.

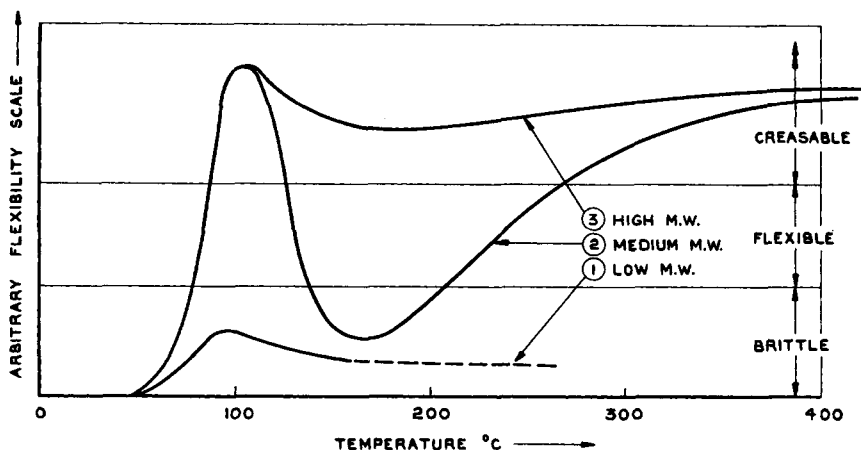


Fig. 5. Effect of molecular weight of poly(amic acid) on film-forming properties.

Solutions of Inherent Viscosity >1.0 ($n > 100$). These gave amber, flexible films in the intermediate stage, which were readily separated from the casting plate. There was very little change in properties following final cure.

Molding Techniques*

Attempts to prepare polyimide moldings by an extension of the solution polymerization process were unsuccessful. Precipitation of the poly(amic acid) from dimethylformamide gave a fibrous plasticized material that could not be efficiently extracted. Attempts to mold the precipitate under a wide range of conditions led to the formation of a shattered mass. X-ray diffraction photographs indicated that this form of the polyimide possessed a higher crystallinity than that of the films and powders.

A suitable molding powder was prepared by development of the tetrahydrofuran precipitation reaction described earlier. The physical form of the poly(amic acid) prepared by this route and the labile nature of tetra-

* Subject of patent applications.

hydrofuran made it possible to extract and dry the product efficiently by using ether or a similar volatile fluid. Tetrahydrofuran and to a lesser extent dioxane were the only solvents which satisfied the requirements of the process, i.e., they were (1) volatile and nonreactive, (2) capable of dissolving both reagents, and (3) nonsolvents for the high molecular weight poly(amic acid), nevertheless allowing extensive polymerization before precipitation occurred.

With the very soluble diamines it was unnecessary to dissolve the components before reacting to form the poly(amic acid), e.g., stoichiometric quantities of diaminodiphenylmethane and PMDA were ground together in a dry box and portions added to stirred anhydrous tetrahydrofuran at 20°C. Dissolution, reaction, and precipitation occurred in rapid succession to give a thick, cream-colored mass of the poly(amic acid). After 5 hr. the tetrahydrofuran was filtered off under dry nitrogen, the product washed with dried ether, and extracted with ether refluxing over phosphorus pentoxide for 4 hr., followed by vacuum drying at 40–50°C. for 1 hr. The poly(amic acid) was in the form of aggregates that easily broke down to particles of 0.025–0.030 in. diameter. The inherent viscosity measured on 0.5% solutions at 30°C. was between 0.5 and 1.0. The higher viscosity samples gave better moldings, as they showed less tendency to embrittlement.

All samples, except those of high inherent viscosity obtained from diaminodiphenyl ether, required a premolding heat treatment of 30 min. at 180°C. After pretreatment the powder was poured into a mold and held under 500 lb./in.² pressure while heating to 200–220°C.; pressure was then increased to 1000–2000 lb./in.² for 1 min. and finally raised to 4000–6000 lb./in.² for a further 10 min. After molding, the samples were heated at 250°C. for several hours to complete the cyclization.

For a final conditioning treatment they were heated to 350–400°C., a pressure of approximately 500 lb./in.² being applied to prevent blistering through loss of volatiles. As in the case of films the high temperature treatment was necessary to give the maximum mechanical properties.

CONCLUSIONS

By careful control of the polymerization conditions it is possible to obtain high molecular weight polyimides with good thermal and mechanical properties. The requirements include a reactive diamine without substituents in the *N*-, *o*-, or *m*- positions and a structure of the type $\text{NH}_2\text{—C}_6\text{H}_4\text{—X—C}_6\text{H}_4\text{—NH}_2$ (preferably 4,4'-substituted), where X itself is thermally stable. It is then necessary to use a polymerization technique which minimizes hydrolytic effects, giving high molecular weight poly(amic acids) with inherent viscosities of 2.0–2.5 in solution polymerization and 0.5–1.0 in precipitation polymerization. Because of degradation it is advisable to use the acid soon after preparation or to store it at 0°C. or below.

Consistently strong films are obtained by using the minimum cure in the range 100–150°C. necessary to drive off solvent and cyclize most of the groups, followed by a short heat treatment at 400°C. Films which are difficult to handle, from diamines such as diaminobenzophenone and *m*- or *p*-phenylenediamine, require chemical cyclization of the poly(amic acid) with an acetic anhydride–tertiary amine mixture to give the best results.

Moldings are most easily prepared by using the powder obtained from precipitation polymerization.

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Résumé

On a préparé des polyimides aromatiques à partir de dianhydride pyromellitique et d'un certain nombre de diamines aromatiques. On a étudié l'effet d'un certain nombre de variables sur la polymérisation et sur la dégradation des acides pyromellitiques intermédiaires; on a mis également en évidence l'existence d'une nouvelle réaction intermédiaire. Au départ de ces études, on a pu définir des conditions nécessaires à l'obtention de poids moléculaires élevés. On a développé des techniques pour fabriquer des films et des moulages satisfaisants.

Zusammenfassung

Aromatische Polyimide wurden aus Pyromellitsäuredianhydrid und einer Anzahl von aromatischen Diaminen dargestellt. Den Einfluss gewisser Variablen auf die

Polymerisation zu den intermediären Polypyromellitamidsäuren und ihren Abbau wurde untersucht und ein bisher nicht bekanntes Reaktionszwischenprodukt wurde isoliert und identifiziert. Anhand dieser Untersuchungen konnten die zur Erreichung hoher Molekulargewichts notwendigen Bedingungen festgelegt werden. Verfahren zur Erzeugung zufriedenstellender Filme und Formteile wurden entwickelt.

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